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Immobilization of N, S-codoped BiOBr on glass fibers for photocatalytic degradation of rhodamine B



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ABSTRACT

Aiming at effectively utilizing visible light and convenient separation of the photocatalysts from the watertreatment system, the N + S-codoped BiOBr photocatalysts with a three-dimensional (3D) open porous structure and visible-light photocatalytic performance have been immobilized on the surface glass fibers (GFs) by a facile solvothermal route. The morphologies and structure of the resultant samples were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT). The as-prepared samples exhibited excellent photocatalytic activities for degradation of rhodamine (RhB) under visible light irradiation. More than 98% RhB can be removed after irradiation for 60 min under visible light. Furthermore, this hybrid material can be easy to separate from the water-phase system. This research provides a new route to access a visible-light induced and convenient separation photocatalyst with a high activity under mild conditions.

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1. Introduction

Bismuth oxybromide (BiOBr), a semiconductor material with the unique sandwich-like tetragonal matlockite structure, a layered structure composed of $[Bi_2O_2]^{2+}$ layers interleaved with double Br layers to form a [Bi₂O₂Br₂] layer unit is the basic material for solving water pollution [1-5]. Although BiOBr was only discovered very recently, it has received great interest since it could provide an excellent object for physics and material science. It combines unique and excellent electrical and optical properties; thus, it has been considered as one of the most promising materials candidate for future photocatalytic degradation under visible-light [6–8]. To promote the practical application of the BiOBr photocatalyst, more effective BiOBr-based photocatalysts are needed. Thus, modulation of its optical-electrical properties is of great technological importance [9-12]. Doping is a common approach to tailor the optical-electronic properties of the semiconductor materials [13–16]. Theoretical studies show that the substitutional doping can modulate the band structure of semiconductor materials [17-19]. For instance, the biggest advantage for N-doped TiO₂ nanoparticles (NPs) is their lower excitation energy compared to pure TiO₂ NPs, which not only allows the absorbance of the UV portion of solar light, but also the visible portion of the solar spectrum [20]. It has also been confirmed in our previous experimental results that Ti-doped BiOBr [21], Fe-doped

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BiOBr [22], Mn-doped BiOBr [23] and S-doped BiOBr [24] exhibited outstanding activities under visible light irradiation. They all showed that the optical response of doped BiOBr could have a red shift and the band gap of the doped BiOBr could be narrow. It has been recognized that codoping could greatly improve the photocatalytic activity which could be ascribed to the synergistic effects of the dopants. Recently, nonmetal or metal codoped TiO₂ had also been extensively explored for visible-light photocatalysis [25–28]. However, a few reports had recently been made to incorporate nonmetal dopants (N, S, and C) into BiOBr nanocrystals. The codoping of dopants into BiOBr nanocrystals can reduce the recombination centers because codoping can passivate the defect bands produced by monodoping. Therefore, the codoped BiOBr nanocrystals could be more desirable for an enhanced photocatalytic performance under visible-light illumination.

As it is well known, immobilization of nanostructured materials on certain substrates to form an ordered structure without agglomeration can improve their handling and transport abilities of the resulting systems. In contrast to fine divided powders, the use of supported materials may avoid losses in flow system applications [29–32]. Nowadays, several methods have used carbon fibers (CFs) as substrate for preparation of composite photocatalysts. These composites showed effective photocatalytic performance and convenient separation of them from the water-treatment system [33–37].

Here, we introduce glass fibers (GFs) as a substrate for growing N + Sdoped BiOBr because of their high aspect ratio, low cost and relative chemical inertness and thermal stability [38–40]. The doped BiOBr nanosheets were immobilized on GFs through a facile solvothermal route and resultant composite photocatalysts showed excellent photocatalytic

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Fig. 1. SEM images of N, S-doped BiOBr/GFs at low (A) and high (B) magnifications, TEM image of N, S-doped BiOBr/GFs (C) and selected-area electron diffraction (SAED) patterns (D).

activity for degradation of rhodamine B (RhB) under visible-light irradiation.

2. Experimental

2.1. Preparation of materials

GFs were firstly activated by NaOH solution (5%) treatment. Doped BiOBr nanosheets were immobilized on the surface of GFs by a solvothermal route. In a typical synthesis, $Bi(NO_3)_3$ + $5H_2O$ (1.0 g) was added to 60 mL 2-methoxyethanol. Urea (0.5 g), thiourea (0.05 g) and CTAB (0.60 g) were added and stirred until a homogeneous solution was obtained. Then, the solution was transferred to a Teflon-lined stainless steel autoclave. The alkali treated GFs were immersed in the solution. The solvothermal synthesis was conducted at 180 °C for 48 h. After cooling, the as prepared samples were washed by water, and dried at 60 °C for 12 h to get the doped BiOBr/GFs products.

2.2. Characterization

The ULTRA-55 field-emission scanning electron microscopy (FE-SEM) at an accelerating voltage of 10 kV and JSM-2100 transmission electron microscopy (TEM) were used to characterize the morphologies of the as-prepared samples. The microstructures and crystal phase of the as-prepared samples were analyzed with a SIEMENS Diffraktometer D5000 X-ray diffractometer with Cu K α radiation source at 35 kV, with a scan rate of 10° s⁻¹ in the 2 θ range of 10–80°. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. The Brunauer-Emmet-Teller (BET) specific surface area was measured using a specific surface & pore size analysis instrument (3H-2000PS1/2 static volume method, China). The photoluminescence (PL) spectra were texted by a HITACHI F-4600 fluorescence spectrophotometer. The calculations are performed with the Cambridge Serial Total Energy

Package (CASTEP) code of Vienna Ab-initio SimulationPackage (VASP) based on the density functional theory (DFT). The concentration of RhB was measured by a JASCO V-570 UV–vis-NIR spectrophotometer (Japan).

2.3. Measurement of photocatalytic activity

The photocatalytic activity of the products was investigated by the photodegradation of RhB. The photodegradation experiments were carried out in a closed box. The radiation source was 500 W high-pressure Xenon lamp without filter which optical power density is 100 mW/cm², and the wavelength of light (λ) was 400–780 nm to simulate the sun light (model BL-GHX-V, Shanghai Bilon Instruments Factory, China). For the photocatalytic degradation of RhB, 0.3 g of the as-prepared catalysts was suspended in a 50 mL RhB ($C_0 = 10 \text{ mg L}^{-1}$) aqueous solution with constant stirring. Prior to irradiation, the suspensions were



Fig. 2. XRD patterns of original GFs and doped BiOBr/GFs.

stirred in the dark for 3 h to ensure the adsorption–desorption equilibrium. For the comparison, a blank experiment (without any catalysts) and a parallel test in the dark (with N, S-doped BiOBr/GFs) were carried out for indicating the adsorption of RhB under the same conditions. Three comparison experiments (with pure GFs, pure TiO₂ (P-25, ~20 nm) and N-doped doped BiOBr/GFs) were also carried out under the same conditions for demonstrating superior performance of N, S-codoped BiOBr under light irradiation. The change of RhB concentration (C_t) in accordance with the irradiation time was measured by a UV–vis-NIR spectrophotometer. The degradation rate could be expressed as the following formula.

Decolonization rate of RhB : $R = (C_0 - C_t)/C_0 \times 100\%$

3. Results and discussion

The morphology and structure of the products are firstly investigated by field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1A shows the SEM image of doped BiOBr/GFs with 0.2 g urea and 0.05 g thiourea as doped resource. Compared with the smooth surfaces of the pure GFs (Fig. 1S), a rough layer is covered onto the surface of GFs. Further investigation by the highmagnification SEM image, the surfaces of GFs are actually composed of many nanosheets (see Fig. 1B) forming a three-dimensional (3D) open porous structure. The thickness of these nanosheets mostly is only ~10 nm. It should be stressed that such small sizes of these nanosheets may be indicative of a possible quantum confinement effect for the properties of such structures. The TEM image of doped BiOBr/GFs



Fig. 3. The high-resolution XPS spectra of Bi4f + S2p (A, C and E), N1s (B, D and F) over undoped and doped BiOBr/GFs.



Fig. 4. Photoluminescence (PL) emission spectra of BiOBr, N, S-codoped BiOBr and N, S-codoped BiOBr/GFs.

is shown in Fig. 1C. It can be founded that the GFs are covered by spindle-like nanosheets with ~50 nm in width and ~100 nm in length at the inner layer and round nanosheets with a diameter at ~150 nm at the outer layer. It suggests that the continuous nanosheets were immobilized simultaneously on GFs and connected together as they continued to grow. Selected area electron diffraction (SAED) pattern taken from the edge of the nanosheets is shown in Fig. 1D. It reveals that the sample has a poly-crystalline nature. Adjusting the mass ratio of urea and thiourea at preparation step, different morphology and structure of the products can be obtained. The GFs covered by nanosheets stilled can be formed with only using urea as doped resource (see Fig. S2). Further increasing the mass of thiourea, the compact structure is breakdown. Adding 0.5 g thiourea and 0.2 g urea as doped resource, a layer with porous and fluffy structure can be formed (see Fig. S3). However, no nanosheets can be formed only using thiourea as doped resource (see Fig. S4). Many nanorods with ~20 nm in diameter and ~2 µm in length are covered on the surface of GFs. It also suggests that the doped resource plays an important role for formation of a compact structure.

Fig. 2 shows the XRD results for original glass fiber and doped BiOBr/ GFs. No clear peaks can be found for pure GFs. The XRD pattern for the doped BiOBr/GFs also exhibits some detectable dopant related peaks besides the typical tetragonal structure of BiOBr crystal (JCPDS no. 73-2061) due to the low content and high dispersity of dopants [24]. The chemical composition of the obtained composites was further confirmed by X-ray photoelectron spectroscopy (XPS) measurement. The survey XPS spectra reveal that the samples are composed of Bi, O, Br, Si, N and S elements (see Fig. S5). The spectrum of an undoped sample contains the bismuth 4f doublet peak (Bi $4f_{7/2}$ and Bi $4f_{5/2}$) with binding energy at 158.7 and 164.1 eV, as shown in Fig. 3A. These binding energy values are those of Bi with an oxidation state of 3^+ [41]. It can be observed from Fig. 3C and E that binding energy shifted to a lower value for Bi $4f_{7/2}$ and Bi $4f_{5/2}$ as the N and N + S doping. Although the relative cross section of sulfur is small in comparison to the Bi element, the sulfur peaks are sensitive to the chemical environment. These doped samples contain the bismuth 4f doublet peak in a spectral region that also S2p doublets (~162.6 eV and 157.2 eV) due to S forming Bi-S bonds [42]. Fig. 3B, D and F shows the XPS spectra for the N 1s region of undoped and doped BiOBr/GFs and its fitting curves. It is a broad peak from 396 eV to 403 eV. Deconvolution of the N 1s peak revealed the presence of two peaks with binding energy at 398 eV and 401.5 eV. The N 1s peak localized at ~398 eV can be ascribed to anionic N incorporated in BiOBr crystal lattice, while the peak at 401.5 eV is assigned to the γ -N₂ [43]. In the case of N + S codoped BiOBr/GFs, the higher peak intensity at 398.5 eV implies that more N elements have been incorporated in the BiOBr crystal lattice.

Photoluminescence (PL) emission spectra originating from the recombination of free charge carriers are useful to reveal the migration, transfer and separation of photogenerated charge carriers. As shown in Fig. 4, the broad PL emission spectra are observed for all samples, which could be attributed to the radiative recombination process of self-trapped excitations. [1,9] The pristine BiOBr has a strong PL emission peak. This energy-wasteful charge recombination process of BiOBr can be greatly inhibited by doping with N and S elements as a result of the redistribution of electrons and holes driven by the band offsets. Thus, the intrinsic drawbacks of fast charge recombination in BiOBr can be solved by the construction of structural imperfection, and a better photocatalytic performance of N + S doped BiOBr can be expected.

The photoactivity of the as prepared samples was firstly evaluated by degradation of RhB ($C_0 = 10 \text{ mg L}^{-1}$) under the UV–visible light irradiation and room temperature (T = 300 K), as shown in Fig. 5A. The adsorption of RhB becomes saturated after 3 h for adsorption and desorption equilibrium in the dark, after which the concentration of RhB does not decrease anymore with prolonging time. For the comparison, a blank experiment is firstly carried out for indicating the selfphotodegradation of RhB under the same conditions. It can be found that RhB self-photodegradation is almost negligible under light irradiation in the absence of catalyst. Only slight change of RhB concentration is observed in the presence of GFs, which indicates that pure CFs do not possess photocatalytic activity except the adsorption. No great change of RhB concentration can be detected in the presence of N, S-codoped BiOBr/CFs in the dark, which indicates that the product does not exhibit



Fig. 5. Photocatalytic degradation of RhB (A) and cycling runs for the photodegradation of RhB (B) over as-prepared products.

photocatalytic activity without light irradiation. In the case of pure-TiO₂, the decolorization rate of RhB is around 15% due to its lower photocatalytic activity under the visible light irradiation range. Compared with the experiments mentioned above, the decolonization rate of RhB is accelerated in the presence of doped BiOBr/GFs, especially the N, Scodoped BiOBr/CFs sample. After irradiation for 60 min, the decolonization rate of RhB is more than 98.5%, which is also higher than that of other reported N-doped TiO₂ systems (~80%) [44,45]. There is no doubt here that codoped BiOBr/GFs play an important role to decolor RhB besides photolysis and adsorption. The improvement of the photocatalytic activity by codoping of dopants into BiOBr nanocrystals can be contributed to the synergistic effects of the dopants, which can passivate the defect bands produced by monodoping and reduce the recombination centers [25–28]. The appearance of codoped BiOBr on the surface of GFs enlarges its specific surface area, and thus, increasing the RhB adsorption capacity. In order to test the re-use performances of composite photocatalyst, the N, S-doped BiOBr/GFs photocatalyst is used to take the recycle photocatalytic decoloration of RhB solution, as shown in Fig. 5B. The efficiency of photocatalytic decoloration is still maintained even after the fifth cycle. The excellent reuse performance of the composite may be resulted from the good binding property between N, S-doped BiOBr nanosheets and GFs.

For investigation of the plausible reaction mechanism for the superior photocatalytic activity of N, S-doped BiOBr/GFs and detecting the active species during photocatalytic reactivity, the hydroxyl radicals (•OH), e superoxide radical (O_2^{-}) and holes (h +) were investigated by adding 1.0 mM isopropyl alcohol (IPA, a quencher of •OH), pbenzoquinone (BQ, a quencher of O_2^{-}), and triethanolamine (TEOA, a quencher of h^+), respectively (see Fig. S6) [11]. The trapping experiments were similar to the photocatalytic activity test above. It can be seen that the photocatalytic decoloration of RhB is declined slightly by the addition of 1 mM IPA. However, after addition of 1 mM BQ or 1 mM TEOA into the reaction system, the decolorization rate of RhB is declerated significantly. Therefore, it can be concluded that O_2^{-} and h^+ are the main active species for decolorization of RhB solution under visible light irradiation, rather than •OH.

To investigate the electronic properties of the as-prepared samples, the band structures of BiOBr and N + S codoped BiOBr crystals with the same energy range of -25-10 eV are firstly calculated, as shown in Fig. 6. The Fermi energy E_f is set at 0 eV. The calculated minimum indirect band gap of N + S-codoped BiOBr is 1.74 eV between valence band maximum (VBM) around the *R* point (0.0 eV) and conduction

band minimum (CBM) at the *Z* point (1.74 eV, Fig. 6B) while the calculated minimum indirect band gap of pure BiOBr is 2.19 eV (Fig. 6A). It is well known that the indirect band gap semiconductor helps to obtain excellent photocatalytic activity because the excited electrons must be emitted to conduction band by traveling certain *k*-space distance, which reduces the recombination probability of the photogenerated electrons and holes. N + S doping can improve the separation of photo-excited carriers due to the formation of impurity energy levels [46].

The total density of states (TDOS) and partial density of states (PDOS) for N + S-doped BiOBr crystal are shown in Fig. S7. The appearance of a small part of N and S states in VB could weaken the localization and broaden the width of VB. It indicates that the doping with elements has the effect on the excited state density of Bi and Br. Furthermore, the doped N and S also can provide excited electrons for the photocatalysis. On the basis of our experiment results and reported literatures [47–49], the possible photocatalytic mechanism of the N, S-doped BiOBr/GFs photocatalysts is proposed. Under the visible light irradiation, the photogenerated holes and electrons are in the valance band and conductance band, respectively. The doped N and S can reduce the bandgap of BiOBr, which can make the easy transition of electrons, resulting in improved photocatalytic performance. The photogenerated holes and O_2^{-} have a strong oxidation potential and serve as active sites responsible for RhB photodegradation.

4. Conclusion

In summary, the N, S-codoped BiOBr nanosheets with visible-light photocatalytic properties have been immobilized on the surface GFs by a facile solvothermal route. The morphologies, structure and photocatalytic activities of the resultant samples were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The differences of the physicochemical properties of the samples have been comparatively analyzed by tests and theoretical calculations in detail. The as-prepared composites exhibited higher photocatalytic activity by evaluation of the decolorization rate of RhB compared with other photocatalytic materials under visible light irradiation. This work may provide new insights into preparing other inorganic photocatalytic fibers for improving their handing capacity and may extend their potential applications for degradation of other organic pollutants.



Fig. 6. The band structures of BiOBr (A) and N + S codoped BiOBr (B) crystals.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.powtec.2014.04.042.

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